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Organic Reagents in Analytical Chemistry Ethylenediaminetetracetic Acid (EDTA)

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In recent years, much has been written in an attempt to classify the reactions of organic reagents with the various metal ions. Analytical chemists have come to associate certain organic structures with a more or less specific ability to react with one or more metal ions. The conception of the dioxime structure as being the nickel-sensitive grouping serves as perhaps the most familiar illustration.

During the past several years, Schwarzenbach and his associates have published a series of papers dealing with complexing reagents of extraordinary potency to which they have given the name "Complexones." The most familiar of these, and possibly the most useful, is ethylenediaminetetracetic acid, henceforth referred to in this paper as EDTA. This remarkable compound, by virtue of its multiplicity of functional groups in close juxtaposition, forms exceedingly stable complexes with a large number of metal ions. Thus, its chemistry is characterized by the large number of metals for which it possesses an affinity rather than the quality of specificity upon which our interest usually is focused. In an earlier issue of *Organic Chemical Bulletin*, Henn (1) discussed the complexes which calcium forms with EDTA and related compounds.

Technology has been quick to apply

EDTA to its own ends. This reagent has been used in a variety of ways to complex metals in process materials and products. Since the complexes are very stable, even traces of metals may be removed effectively, in many cases, merely by adding the reagent. The analytical chemist has been somewhat slower in giving the chemistry of this compound the attention it deserves. Since the metal complexes possess varying degrees of stability and their stability may be altered by changing the pH of the medium, considerable specificity may be achieved by proper manipulation of experimental conditions.

Masking Reagents

Přibil and Sedlár (2), for example, have shown how EDTA can be used to separate tungsten from iron, copper, and aluminum by the 8-hydroxyquinoline (oxine) method. At pH = 5, which is optimum for the precipitation of tungsten, this reagent also precipitates copper, aluminum, and trivalent iron quantitatively. In the presence of EDTA, only tungsten is precipitated. After the tungsten is removed, iron and copper may be quantitatively precipitated from the filtrate as oxinates, simply by raising the pH with ammonia. Obviously, the stability of the oxinates of these metals

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is increased to a greater extent than that of the EDTA complexes by raising the pH. Aluminum precipitates only partially from ammoniacal solution under these conditions.

A further example, also from Přibil and Sedlář, of manipulation in the oxine scheme of analysis is provided by a suggested separation of tungsten from cobalt. In the presence of EDTA, only tungsten is precipitated at $\text{pH} = 5$. Upon raising the pH to 8 – 9 and adding an amount of calcium equivalent to the EDTA, the cobalt is liberated from its complex and is precipitated quantitatively as the oxinate. This is an interesting case in which a metal forming a complex of high stability is used to decompose an EDTA complex of much lesser stability.

Method for Water Hardness

Perhaps the best known analytical application of EDTA, based on its ability to form complexes with calcium and magnesium, was first suggested by Schwarzenbach, with Biedermann (3,4) and with Bangerter (5). These workers showed (4) that the blue dye, Eriochromeschwarz T, forms a deep wine-red compound with calcium and magnesium and may be used as an indicator for titrating these ions with EDTA. The obvious application as a method for determining total hardness of water was quickly and generally accepted. A number of American investigators, notably Betz and Noll (6) and Diehl, Goetz, and Hach (7), made further refinements in the method. Goetz, Loomis, and Diehl (8) showed that standard EDTA solutions are relatively stable, changing less than 1 percent in strength in 4 months under optimum pH conditions.

Ammonium purpurate forms a red complex with calcium but not with magnesium (5) and thus may be used as an indicator for the determination of calcium hardness in the presence of magnesium, since calcium forms the more stable complex with EDTA and reacts

with it first. Munger, Nippler, and Ingols (9) showed that Eriochromeschwarz T gives a deep-colored complex with barium which serves as the basis of a volumetric method for sulfate. Excess barium is added and back-titrated with standard EDTA solution.

Potentiometric Titrations

Only a relatively few instances are known in which complexing agents can be used to produce a potential change in a redox system corresponding to an endpoint. An interesting example has very recently been provided by Přibil, Koudela, and Matyska (10), in which EDTA is used to titrate ferric iron to a potentiometric endpoint.

The potential of a platinum electrode in a solution containing an oxidized and reduced form of an element is given by the familiar Nernst equation,

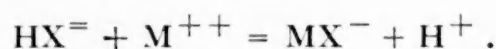
$$E = E_0 + 0.059 \log \frac{[\text{OX}]}{[\text{RED}]}$$

If a complexing agent is added to a solution of the oxidized form, containing a small amount of the reduced form, and if the complex of the oxidized form is much more stable than that of the reduced form, it follows that an abrupt change in the ratio, $[\text{OX}]/[\text{RED}]$, will occur at the stoichiometric point. The resulting change in potential is directly related to the ratio of the stability constants of the complexes. In the case of the titration of iron with EDTA, ΔE may amount to as much as 350 millivolts per 0.04 milliliter of $N/10$ solution at the optimum pH of 5. A useful potential jump is also obtained with the system, $\text{Cr}^{+++}/\text{Cr}^{++}$.

The reverse titration of EDTA with a standard ferric iron solution containing a trace of ferrous iron is also possible. This permits the indirect determination of cations, such as nickel, copper, zinc, cadmium, and lead, which form more stable complexes than iron. An excess of EDTA is added and the excess is back-titrated with standard iron solutions to a potentiometric endpoint.

Alkalimetric Methods

Among the numerous complexones described by Schwarzenbach and Biedermann (11) is nitrilotriacetic acid, $N(CH_2COOH)_3$, which was designated as Complexone I, and which also forms complexes with many of the cations. (*Chemical Abstracts* lists this compound as "acetic acid, trinitrilo.") By adding successive equivalents of alkali, each of the three acidic hydrogens of this compound can be neutralized, yielding the mono-, di-, and tripotassium or sodium salts, respectively. The titration curve shows three distinct jumps in pH, as might be expected for a tribasic acid, with a pH value of approximately 5.5 corresponding to the dipotassium salt. The reaction between this reagent and the various metal ions proceeds on a 1-to-1 molar basis, according to the following equation, where HX^- represents the anion corresponding to the dipotassium salt, K_2HX .



The liberated hydrogen ion causes a sharp decrease in the pH of the solution, and this acid may be titrated with potassium hydroxide to an entirely satisfactory endpoint which coincides very nearly with the pH of the K_2HX reagent.

The tripotassium salt may be used in very much the same manner. In this case, one, in effect, adds the dipotassium salt and the standard potassium hydroxide solution simultaneously. The pH changes very little throughout the course of the titration but rises abruptly at the endpoint, since the unreacted reagent is alkaline by hydrolysis. Solutions of cadmium, cobalt, copper, divalent iron, mercury, manganese, lead, nickel, zinc, cerium, and lanthanum may be titrated in this manner.

The di- and tripotassium salts of EDTA may be used in a manner exactly analogous to dipotassium hydrogen triacetate (12). Although the tetrapotassium salt of EDTA behaves much like

tripotassium nitrilotriacetate, its use suffers from the practical disadvantage that traces of free alkali diminish the pH rise at the endpoint and traces of free acid make it necessary to apply an endpoint correction.

Polarographic Applications

The formation of complexes between the various metal ions and EDTA may significantly alter their polarographic behavior. The half-wave potentials of many of the metals are shifted to more negative values by the presence of the complexing agent, and the magnitude of the shift is, in general, proportional to the stability of the metal complex. In the case of some cations, such as nickel and zinc, which have highly negative deposition potentials and which form very stable complexes with EDTA, the shift in half-wave potential is so large that, for all practical purposes, their polarographic waves do not exist. Furness, Crawshaw, and Davies (13) have described this shift in the polarographic waves of copper and iron and have utilized the wave of the copper complex as the basis of a method for determining EDTA. Přibil (14) states that the lead wave may be shifted as much as one volt, depending upon the pH of the medium. Since thallium does not form a stable complex with EDTA, it is possible to determine this element polarographically in the presence of copper, and especially lead, which would normally interfere with the thallium determination.

In addition to its usefulness in separating the polarographic half-waves of some of the metals, the potential shift may also be made to serve as the basis of amperometric methods in which EDTA is used as the titrating reagent (14). An electrode potential is chosen at which the simple cation is reduced but its EDTA complex is not. As the reagent is added, the diffusion current decreases until the endpoint is reached. Further additions of reagent produce no further

change in the current.

The analytical possibilities of Schwarzenbach's "Complexones" are, as yet, largely unexplored. The illustrations given here serve to show that they are interesting and useful compounds worthy of the attention of the analytical chemist.

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	$(C_2H_5)_2NCH_2CHOHCH_2NH_2$. . . MW 146.23	
P 6618	N-(2-Aminoethyl)morpholine (Pract.) BP 96-97°/20mm.500 g. . .	4.45 E
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